GROUP III ANALYSIS

(Al^{3+}, Cr^{3+}, Fe^{3+})

The group III cations are grouped together because they can all be separated from solution as insoluble hydroxides in buffered alkaline solutions. Group III cations are easily identified by color. Cr^{3+} is blue-purple, Fe^{3+} is yellow as a chloride, and Al^{3+} is clear.

SEPARATION AND IDENTIFICATION OF GROUP III IONS: (Reactions)

1. Group III cations are separated from solution as hydroxides from a buffered alkaline solution of NH_4Cl and NH_3:

$$NH_3 + H_2O \text{ -----> } NH_4^+ + OH^-$$

$$M_3^+ + 3\,OH^- \text{ ----> } M(OH)_3$$

where $M^{3+} = Al^{3+}$, Fe^{3+}, Cr^{3+}

The ammonia solution used for precipitation must be buffered with NH_4Cl in order that the OH- concentration will be low enough that other groups will not precipitate.

2. Both $Al(OH)_3$ and $Cr(OH)_3$ dissolve in excess NaOH as a result of soluble hydroxo-complexes. $Fe(OH)_3$ is insoluble in excess NaOH:

$$Al(OH)_3 + OH^- \text{ ----> } Al(OH)_4^-$$

$$Cr(OH)_3 + 3\,OH^- \text{ ----> } Cr(OH)_6^{-3}$$

Hydroxo-complexes of chromium decompose upon heating to form insoluble $Cr(OH)_3$, but $Al(OH)_4^-$ does not decompose on heating. Therefore, aluminum may be separated from iron and chromium by addition of NaOH to the hydroxide precipitate in a hot mixture.

3. The presence of Al^{3+} is confirmed by decomposing $Al(OH)_4^-$ with nitric acid followed by precipitation of $Al(OH)_3$ with ammonia:

$$Al(OH)_4^- + 4\,H^+ \text{ ----> } Al^{3+} + 4\,H_2O$$

$$Al^{3+} + 3\,OH^- \text{ ----> } Al(OH)_3$$

4. The chromium ion is separated from iron by oxidation of $Cr(OH)_3$ to CrO_4^{2-} with H_2O_2 in strongly basic solution:

$$2\ Cr(OH)_3 + 3\ H_2O_2 + 4\ OH^- \text{----> } 2\ CrO_4^{2-} + 8\ H_2O$$

5. The yellow chromate ions are converted to orange dichromate ions in an acidic solution:

$$2\ CrO_4^{2-} + 2\ H^+ \text{-----> } Cr_2O_7^{2-} + H_2O$$

When H_2O_2 is added an acidic dichromate solution, blue chromium peroxide, CrO_5 is formed:

$$Cr_2O_7^{2-} + 4\ H_2O_2 + H^+ \text{----> } 2CrO_5 + 5\ H_2O$$

The blue color disappears because unstable CrO_5 rapidly decomposes to form Cr^{3+}.

6. The presence of iron is confirmed by dissolving $Fe(OH)_3$ in hydrochloric acid and adding NH_4SCN to form the blood red thiocyanate complex, $Fe(SCN)^{2+}$:

$$Fe(OH)_3 + 3\ H^+ \text{-----> } Fe^{3+} + 3\ H_2O$$

$$Fe^{3+} + SCN^- \text{-----> } Fe(SCN)^{2+}$$

EXPERIMENTAL PROCEDURE: (Group III)

1. **Separation of Group III**
   A. Obtain 2-3 ml of Group III solution or use the decantate from step #1D in Group I if doing unknowns.
   B. Add 4 drops of 3M NH_4Cl to the test solution.
   C. Add drops of 6M NH_3 until <u>just barely</u> basic.
   D. Centrifuge, test for complete precipitation, and repeat step B if necessary.
   E. Add 10 drops of water, mix <u>thoroughly</u>, centrifuge, and decant.
   F. <u>Save the precipitate</u> and discard the decantate. (**IMPORTANT NOTE**: Save the decantate for group IV analysis when doing unknowns.)

2. **Separation of aluminum**
   A. Wash the precipitate with 2 drops of 6M NH_3 and 8 drops of H_2O. Centrifuge. Discard decantate.
   B. Add 6 drops of 6M NaOH. Heat for 5 minutes. Mix thoroughly while heating.
   C. Centrifuge. If supernatant is not clear and colorless, heat for several more minutes and centrifuge. Be careful not to jiggle tube when removing from centrifuge. Precipitate remixes easily.
   D. Decant. Save precipitate for step #4. Save decantate for step #3.

3. **Confirmation of aluminum**
   A. Add drops of 6M HNO_3 to the decantate until acidic
   B. Add drops of 15M NH_3 until basic.
   C. Centrifuge, and decant. Presence of a white precipitate is a positive test for aluminum. Precipitate may be very slight and fluffy.
   D. Since aluminum is sometimes difficult to detect a further confirmation test may be necessary: Add 10 drops of 6M acetic acid to the solution and heat in a hot water bath for 2-3 minutes. Discard any undissolved residue. Add 10 drops of 3M ammonium acetate. Add 5 drops of 0.1% aluminon and mix thoroughly. Add 15M ammonia dropwise until the solution is basic. A bright red precipitate at this point will confirm the presence of aluminum.

4. **Separation of chromium**
   A. Add 4 drops of 6M NaOH and 10 drops of 3% H_2O_2 to the precipitate from step 2D.
   B. Heat in a water bath until O_2 evolution ceases. Continue to heat for 1 minute after oxygen evolution ceases.
   C. Add 10 drops of H_2O, centrifuge, and decant. Save both the decantate and precipitate.

5. **Confirmation of chromium**
   A. Using the decantate from step #4C, heat for one minute.
   B. Add drops of 6M HNO_3 until acidic.
   C. **RAPIDLY**, squirt in a shot of 3% H_2O_2. Look quickly and carefully for a color change.
   D. Presence of blue color is a positive test for chromium. NOTE: This compound and color is unstable and decomposes rapidly.

6. **Confirmation of iron**
   A. Use the precipitate from step #4C. Wash it with 10 drops H_2O. Centrifuge and decant. Discard the decantate.
   B. Add drops of 6M HCl to the solid until it is completely dissolved.
   C. Add 2 drops of 1M NH_4SCN. Presence of a blood red color is a positive test for iron. Only a deep red color confirms the presence of iron. A faint red/pink may be the result of contamination.

NOTE - YOU MUST PREPARE YOUR OWN FLOW CHART FOR USE WHEN YOU DO YOUR UNKNOWN.

Group III solution or Decantate from Group I if doing unknowns

/ +4 3 M NH_4Cl

/ +n 6 M NH_3 until basic,

/ c, t, rii.

/ +10 H_2O, c, d.

SEP. OF Aluminum

PPT GROUP III IONS

decantate for group III if doing unknowns otherwise discard

/ w +2 6M NH_3, +8 H_2O, c, discard decantate.

/ +6 6M NaOH, h-5, c.

/ is decantate clear? if not, heat for 3 minutes, c, d.

* be careful, precipitate mixes easily.

Sep. of Chromium Confirmation

PPT Fe^{+3} Cr^{+3}?

/ +4 6M NaOH, +10 H_2O_2

/ h-n until gas bubbles stop

/ h-1 minute more

/ +10 H_2O, c, d

Confirmation of Al

DECANTATE Al?

/ +6 6M HNO_3 until acidic (blue → red)

/ +n 6M NH_3 until basic

/ if yellow add 6B size NH_4I

/ c, d.

Conf. of Fe

PPT.

/ w +10 H_2O, c, d.

throw decantate

ppt. only

/ +4 6M HCl until dissolved

/ +2 1 NH_4SCN

Blood Red color is positive

decantate

Conf. of Chromium

/ h-1

/ +n 6M HNO_3, til acidic

/ +5 H_2O_2

look quickly for blue color

If yes

Cr

if white precipitate Al is present

further test for Al

/ +10 6M Acetic Ac

/ h-3

discard ppt.

Decantate

/ +10 3M Ammonium Acetate

/ +5 Aluminon

/ +n NH4 til ba

BRIGHT RED INDICATE